

Appendix

A.1 Statistical Methods for Determining Exposure Concentrations

Sampling results from many environmental investigations reveal that the data are lognormally distributed. If data from a site are lognormally distributed, it may be necessary to transform the data using the natural logarithm function before calculating the 95% UCL of the arithmetic mean for each exposure area. The W-test is one method for determining whether a data set is normally or logarithmically distributed.

After determining the distribution of the data set, the risk assessment should state the 95% UCL concentration of the COCs in each exposure area. The following equations should be used to calculate the 95% UCL:

Equation for calculating the UCL of the arithmetic mean for a normal distribution

$$UCL = \bar{x} + t \left(\frac{s}{\sqrt{n}} \right)$$

Equation - A

where:

\bar{x}	=	mean of the untransformed data
s	=	standard deviation of the untransformed data
t	=	Student-t statistic
n	=	number of samples

Equation for calculating the UCL of the arithmetic mean for a lognormal distribution

$$UCL = e^{\bar{x} + 0.5t^2 + tH\sqrt{\frac{s^2}{n}}} - 1$$

Equation - B

where:

e	=	constant (2.718)
\bar{x}	=	mean of the transformed data
s	=	standard deviation of the transformed data
H	=	H-statistic
n	=	number of samples

Although the geometric mean is a convenient parameter for describing central tendencies of lognormal distributions, it is not an appropriate basis for estimating the concentration term used in risk

assessments since it bears no logical connection to the cumulative intake from long-term contact to contamination at a site (USEPA 1995a).

A.2 Models to Estimate Contaminant Flux

Vapor phase migration of the COCs to the surface may be estimated using diffusion modeling. A number of acceptable mathematical models are presented in the SEAM (USEPA 1988) and the Air/Superfund National Technical Guidance Study Series Document: *Guideline for Predictive Baseline Emissions Estimation for Superfund Sites* (USEPA 1995b). Acceptable approaches vary in complexity. The simple conservative models are easy to use and will take little time use. More complex models will be more difficult to use, but will result in more accurate and less conservative flux estimates. Generally, the decision to use the more complex models will involve balancing the potential remediation costs with the costs of obtaining site-related data, and the additional cost of using the more complicated models (USEPA 1996a).

A.2.1 Karimi (Farmer) Model

A screening-level model has been developed by Karimi et al. (Karimi et al. 1987), which assumes zero concentration of volatilizing material at the soil surface and a non-diminishing and a continuous source of contaminants in a system at equilibrium. The formula assumes that contaminants are present at less than the soil saturation limit. The approach includes conservative assumptions that provide an upper-bound flux estimate. Site-related data that are required include the concentration of contaminants in soil gas, and the thickness of the clean soil layer. Soil properties may assume default values or include site-specific data. The following expression describes the screening-level approach to estimating flux developed by Karimi et al.:

$$J_i = \frac{(D_i)(C_g)(P_a^{3/3}/P_t^2)}{L}$$

Equation - C

where:

J_i	=	Flux rate of component i (mg/m ² •sec)
D_i	=	Diffusion coefficient in air of component i (m ² /sec)
C_g	=	95% UCL concentration in soil gas of component i (mg/m ³)
P_a	=	Air filled porosity of the soil (dimensionless)
P_t	=	Total soil porosity (dimensionless)
L	=	Depth of clean soil cover (m)

A.2.2 Simplified Jury Model

A similar equation has been developed by Jury et al. to estimate vapor flux of volatile compounds from surface soils. The equation estimates the maximum time-averaged diffusive vapor flux and assumes no immiscible phase (NAPL) is present (Jury et al., 1980;1983). The model assumes there is no clean soil layer above the contamination.

$$F_{ss,out} = 2\rho_s C_{ss} \sqrt{\frac{HD^a \frac{\theta_v^{3,ss}}{\theta_T^2} + D^w \frac{\theta_v^{3,ss}}{\theta_T^2}}{\pi(\theta_w + k_s \rho_s + \theta_v H)\tau}}$$

Equation - D

where:

$F_{ss,out}$	=	vapor emissions from surface soil to outdoor ambient air (g/cm ² -s)
C_{ss}	=	surface soil exposure concentration (g/g-soil)
ρ_s	=	soil bulk density (g-soil/cm ³ -soil)
H	=	Henry's Law constant ((g/cm ³ -vapor)/(g/cm ³ -water)
D^a	=	diffusion coefficient in air (cm ² /s)
D^w	=	diffusion coefficient in water (cm ² /s)
θ_w	=	soil moisture content (cm ³ -water/cm ³ -soil)
θ_v	=	soil air porosity (cm ³ -vapor/cm ³ -soil)
θ_T	=	total soil porosity (cm ³ /cm ³ -soil)
π	=	3.14.
k_s	=	soil-water partition coefficient (g/g-soil)/(g/cm ³ -water) =

$$k_s = k_{oc} \times F_{oc}$$

k_{oc}	=	soil organic carbon-water partition coefficient (g/g-soil)/(g/cm ³ -water)
F_{oc}	=	fraction of organic carbon in soil (g/g-soil)
τ	=	exposure interval (s).

A.2.3 Jury Finite Source Model

Jury et al. have developed an equation for estimating the flux of a contaminant from a finite source of contaminated soil (Jury et al. 1990). The model is applicable when contamination extends from the surface for a known fixed thickness in the soil column. The model is applicable when there is no clean soil layer above the contamination. The following assumptions were used to derive this simplified equation:

- Uniform soil properties (homogeneity)
- Instantaneous linear equilibrium adsorption
- Linear equilibrium liquid-vapor partitioning
- Uniform initial contaminant concentration
- Contaminants present at less than saturation
- No clean soil layer

- No water evaporation or leaching
- No biological or chemical degradation

$$J_s = C_o \left(\frac{D_A}{\pi \tau} \right)^{1/2} \left[1 - \exp \left(\frac{-d_s^2}{4D_A \tau} \right) \right]$$

Equation - E

where:

J_s	=	contaminant flux at ground surface (g/cm ² -s)
C_o	=	uniform contaminant concentration at $\tau = 0$ (g/cm ³)
D_A	=	apparent diffusivity (cm ² /s)
π	=	3.14
τ	=	time(s)
d_s	=	depth from the soil surface to the bottom of contamination at $\tau=0$ (cm),

and where:

$$D_A = \frac{\left[\frac{\Theta_a^{10/3} D_i H' + \Theta_w^{10/3} D_w}{n^2} \right]}{\rho_b K_d + \Theta_w + \Theta_a H'}$$

Equation - F

where:

Θ_a	=	air-filled soil porosity (L_{air}/L_{soil}) = $n - \Theta_w$
n	=	total soil porosity (L_{pore}/L_{soil}) = $1 - (\rho_b/\rho_s)$
Θ_w	=	water-filled soil porosity (L_{water}/L_{soil}) = $w \rho_b/\rho_w$
ρ_b	=	soil dry bulk density (g/cm ³)
ρ_s	=	soil particle density (g/cm ³)
w	=	average soil moisture content (g/g)
ρ_w	=	water density (g/cm ³)
D_i	=	diffusivity in air (cm ² /s)
H'	=	dimensionless Henry's law constant = $41 \times H$
H	=	Henry's law constant (atm-m ³ /mol)
D_w	=	diffusivity in water (cm ² /s)
K_d	=	soil-water partition coefficient (cm ³ /g) = $K_{oc} f_{oc}$
K_{oc}	=	soil organic carbon partition coefficient (cm ³ /g)
f_{oc}	=	organic carbon content of soil (g/g)

To estimate the average contaminant flux over 30 years, the time-dependent contaminant flux must be solved for various times and the results averaged. A simple computer program or spreadsheet can be used to calculate the instantaneous flux of contaminants at set intervals and numerically integrate the results to estimate the average contaminant flux. The time-step interval must be small enough (e.g., 1-day intervals) to ensure that the cumulative loss through volatilization is less than the total initial mass. Inadequate time steps can lead to mass-balance violations (USEPA 1996a).

Alternatively, the EMSOFT computer program developed by the USEPA Office of Research and Development National Center for Environmental Assessment (NCEA) may be used to estimate average flux. The computer program provides an average emission flux over time by using an analytical solution to the integral, thereby eliminating the problem of establishing adequate time steps for numerical integration. EMSOFT is available through the NCEA in Washington, D.C.

A.2.4

Another acceptable approach for quantifying flux from soils in equilibrium (ie. no NAPL present) is described below (USEPA 1995b). The equation is applicable when a finite source exists, with a clean soil layer above the contamination. Flux must be calculated for various time periods as in Section A.2.3.

$$F_{i(\tau)} = \beta C_{o,i} \left(\frac{D_{A,i}}{\pi \tau} \right)^{1/2} \left[\exp \left(- \frac{d_c^2}{4 D_{A,i} \tau} \right) - \exp \left(- \frac{(d_c + w_c)^2}{4 D_{A,i} \tau} \right) \right] 0.116$$

Equation - G

where:

$F_{i(\tau)}$	=	Emission flux of component i from subsurface soils at each time-step, g/m ² -s
β	=	Average soil dry bulk density, g/cm ³ - soil
$C_{o,i}$	=	Initial soil concentration of i , g/g-soil
$D_{A,i}$	=	Apparent diffusion coefficient of i in soil, cm ² /d (Equation F)
π	=	3.1416
τ	=	Cumulative time at each time-step, days
d_c	=	Depth from soil surface to top of contamination, cm
w_c	=	Thickness of contaminated soil, cm
0.116	=	Factor to convert g/mc ² -d to g/m ² -s

A.2.5 Infinite Source Models for Surface Soils Containing NAPL

The following model (USEPA 1995b) estimates flux at sites that contain contaminants in excess of soil saturation limits (ie. NAPL may be present). The model operates under the assumption of steady-state conditions and an infinite source (ie. contamination extending from the ground surface to an infinite depth) over the averaging period. The model is applicable when there is no clean soil layer above the contamination.

$$\overline{F}_i = \beta C_{o,i} \left(\frac{2 C_{v,eq} D_{e,i}}{\beta C_{o,i} \tau} \right)^{1/2} 0.116$$

Equation - H

$$C_{v,eq} = \frac{X_i P_i MW_i}{RT}$$

where:

Equation - I

and where:

$$D_{e,i} = \left(\frac{\Theta_a^{10/9}}{\Theta_i^2} D_{a,i} \right) + \frac{1}{H'_i} \left(\frac{\Theta_v^{10/9}}{\Theta_i^2} D_{v,i} \right)$$

Equation - J

where:

F_i	=	Average emission flux of component i from surface soils over exposure averaging period τ , (g/m ² -s)
β	=	Average soil dry bulk density, (g/cm ³ -soil)
$C_{o,i}$	=	Initial soil concentration of i, (g/g-soil)
$C_{v,eq}$	=	Equilibrium vapor concentration when NAPL is present in the soil, (g/cm ³ -vapor) (Equation I)
$D_{e,i}$	=	Maximum effective diffusion coefficient of i when NAPL is present, (cm ² /d) (Equation J)
τ	=	Exposure averaging period, days (for residential land-use τ = 10,950 days)
0.116	=	Factor to convert (g/cm ² -d) to (g/m ² -s)
$C_{v,eq}$	=	Equilibrium vapor concentration of i when NAPL is present, (g/cm ³ -vapor)
X_i	=	Mole fraction of i in the residential mixture, (g/mol per g/mol)
P_i	=	Pure component vapor pressure of i, (mm Hg)
MW_i	=	Molecular weight of i, (g/mol)
R	=	Molar gas constant, 62,361 (mm Hg-cm ³ /mol-°K)
T	=	Average in situ soil temperature, (°K)
Θ_a	=	Air-filled soil porosity unitless

Θ_{τ}	=	Total soil porosity, unitless
$D_{a,i}$	=	Diffusion coefficient of i in air, cm ² /d
H_i	=	Henry's law constant of i, unitless
Θ_w	=	Water-filled soil porosity, unitless
β	=	Average soil dry bulk density, g/cm ³
$D_{w,i}$	=	Diffusion coefficient of i in water, cm ² /d

A.2.6 Infinite Source Models for Sub-Surface Soils Containing NAPL

The following model (USEPA 1995b) estimates flux at sites that contain contaminants in excess of soil saturation limits (ie. NAPL may be present). The model operates under the assumption of steady-state conditions and an infinite source (ie. contamination extending from the ground surface to an infinite depth) over the averaging period. The model is applicable when there is a clean soil layer above the contamination.

$$F_i = \left(\frac{\beta C_{o,i}}{\tau} \right) \left[\left(d_e^2 + \frac{2 C_{v,eq} D_{e,i} \tau}{\beta C_{o,i}} \right)^{1/2} - d_e \right] 0.116$$

Equation - K

where:

F_i	=	Average emission flux of component i from surface soils over exposure averaging period τ , (g/m ² -s)
β	=	Average soil dry bulk density, (g/cm ³ -soil)
$C_{o,i}$	=	Initial soil concentration of i, (g/g-soil)
$C_{v,eq}$	=	Equilibrium vapor concentration when NAPL is present in the soil, (g/cm ³ -vapor) (Section A.2.4)
$D_{e,i}$	=	Maximum effective diffusion coefficient of i when NAPL is present, (cm ² /d) (Section A.2.4)
τ	=	Exposure averaging period, days (for residential land-use $\tau = 10,950$ days)
d_e	=	Distance from soil surface to top of contamination (cm)
0.116	=	Factor to convert (g/cm ² -d) to (g/m ² -s)

A.3 Air Dispersion Modeling for Determining Outdoor Air Concentrations

Developing estimates of outdoor air concentrations from flux estimates will require an air dispersion term. Dispersion into outdoor air may be estimated using a simplified box model, or using a default or site specific value for Q/C.

A.3.1 “Box Model”

The following “box model” also may be used to predict outdoor ambient air concentrations for receptors at the downwind edge of the source area. The model assumes the air is well-mixed within the box and the dimensions of the box are equal to the human breathing zone height and the length of the emission source in the predominant wind direction. Given these assumptions the following equation is used to estimate outdoor ambient air concentrations from vapor emissions flux:

$$C_{a,out} = \frac{F_{out}L}{\delta u}$$

Equation - L

where:

$C_{a,out}$	=	outdoor ambient air concentration (g/cm ³)
F_{out}	=	vapor emissions from soil (surface or subsurface) to outdoor ambient air (g/cm ² -s)
L	=	length of emissions source in the wind direction (cm)
δ	=	height of breathing zone (cm)
u	=	average annual wind speed (cm/s)

A.3.2 Q/C Dispersion Term

Flux may be converted to an outdoor air concentration using the following expression:

$$OAC = \frac{J_i}{Q/C}$$

Equation - M

where:

OAC	=	Outdoor air concentration of component i (kg/m ³)
J_i	=	Flux rate of component i (g/m ² •sec)
Q/C	=	Dispersion term for Phoenix, AZ (64.04 g/m ² •sec per kg/m ³)

The default dispersion term (Q/C) for Phoenix has been derived by the USEPA using the Industrial Source Complex Model (ISC2) platform in both a short-term and long-term modes (USEPA 1996a). The model uses a double numerical integration over the source in the upwind and crosswind directions. Dispersion is quantified using a full year of meteorological data from Phoenix.

A site-specific Q/C term can be determined using the Industrial Source Complex Model platform in the short-term mode (ISCST3). A brief overview of this application, assumptions, and input requirements for the model is provided in the USEPA Soil Screening Guidance Document (USEPA 1996a). The ISCST3 model FORTRAN code, executable versions, sample input and output files, description, and documentation can be downloaded from the "Other Models" section of the USEPA Office of Air Quality Planning and Standards Support Center for Regulatory Air Models bulletin board system (SCRAM BBS). To access this information call:

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A.4 Indoor Air Concentrations

Vapors diffusing through subsurface soils may also enter residential and non-residential structures through cracks and seams in the foundation. Vapor intrusion into enclosed space may be controlled by diffusive and convective transport.

A number of models may be used to flux estimates into contaminant concentrations indoors. The USEPA document entitled *Assessing Potential Indoor Air Impacts for Superfund Sites* (USEPA 1995b) presents many such models. The models that may be vary in complexity, with simpler models providing and upper-bounds estimate.

A.4.1 Simplified Intrusion Model

The following expression (USEPA 1992c) represents a screening-level model that may be used to estimate indoor air concentrations from flux estimates:

$$IAC = \frac{J_i(a)(F)}{(ACH)(CF)(v)}$$

Equation - N

where:

IAC	=	Indoor air concentration (mg/m ³)
J _i	=	Flux rate of component i (mg/m ² ·sec)
a	=	Area of building floor (m ²)
F	=	Fraction of floor through which vapors may enter (dimensionless)
ACH	=	Building air changes per hour (air changes/hour)
CF	=	Conversion factor (2.77E-4 hours/second)
v	=	Volume of building (m ³)

The indoor air concentration is dependent on the fraction of floor through which soil gas may enter, the volume of the building, the number of air changes per hour and the flux. For buildings with slab floors, the fraction of floor space through which soil gas may enter may be assumed to be 0.001 or 0.1% (USEPA 1992c).

A.4.2 Comprehensive Intrusion Model

The following equations convert soil gas concentrations to indoor air concentrations (Johnson and Ettinger 1991). The model assumes a nondiminishing source located at a distance (L) beneath the foundation and a foundation with a thickness equal to L_{crack} to estimate vapor emissions into enclosed spaces:

$$F_{enc} = Q_B C_g \left(\frac{D_s^{eff} A_B}{Q_B L} \right) \frac{\exp\left(\frac{Q_{soil} L_{crack}}{D_{crack} A_{crack}}\right)}{\left[\exp\left(\frac{Q_{soil} L_{crack}}{D_{crack} A_{crack}}\right) + \left(\frac{D_s^{eff} A_B}{Q_{soil} d} \right) \left(\exp\left(\frac{Q_{soil} L_{crack}}{D_{crack} A_{crack}}\right) - 1 \right) \right]}$$

Equation - O

where:

F_{enc}	=	vapor emissions into enclosed spaces (g/s)
Q_B	=	volumetric flow rate of enclosed space (cm ³ /s)
C_g	=	concentration of the chemical in the soil gas (g/cm ³ -vapor)
D_s^{eff}	=	effective diffusion coefficient (cm ² /s)
L_{crack}	=	foundation thickness (cm)
D_{crack}	=	effective diffusion coefficient through foundation cracks (cm ² /s)
A_{crack}	=	area of foundation through which vapors are transported (cm ²)
A_B	=	total area of enclosed space exposed to vapor intrusion (cm ²)
L	=	depth from chemical to foundation (cm)
Q_{soil}	=	volumetric infiltration flow rate of soil gas into enclosed space (cm ³ /s)

The estimated indoor air exposure concentration, dependent upon the volume of air within the enclosed space and the air exchange rate of the space, can then be calculated using the following equation:

$$C_{a,enc} = \frac{F_{enc}}{V_B E_B}$$

Equation - P

where:

$C_{a,enc}$	=	Enclosed space air exposure concentration (g/cm ³)
F_{enc}	=	vapor emissions into enclosed space (g/s)
V_B	=	volume of enclosed space (cm ³)
E_B	=	enclosed space air exchange rate (s ⁻¹)

A.4.3 Johnson and Ettinger Model

Another acceptable model for evaluating vapor intrusion has been developed by Johnson and Ettinger (Johnson and Ettinger 1991). The model is a closed-form analytical solution for convective and diffusive transport of vapor-phase contaminants into buildings. The model is relatively complex, and is not discussed in detail here. Parties wishing to use this model are encouraged to consult the original literature source.

A.5 Estimating Particulate Emissions

In order to calculate chemical concentrations from dust exposures, a respirable particulate emission factor (PEF) must be determined and combined with soil exposure concentrations. The default PEF value may be used or a site-specific estimate may be made using the following expression:

$$PEF(m^3/kg) = Q/C \frac{\frac{3600s}{h}}{0.036(1-V) \left(\frac{U_m}{U_t} \right)^3 F(x)}$$

Equation - Q

<u>Parameter</u>	<u>Definition (units)</u>	<u>Default</u>
PEF	Particulate emission factor (m ³ /kg)	1.316 x 10 ⁹
Q/C	Inverse of the mean concentration at the center of a 0.5-acre-square source (g/m ² -s per kg/m ³)	90.80
V	Fraction of vegetative cover (unitless)	0.5 (or site-specific)
U _m	Mean annual windspeed (m/s)	4.69 (or site-specific)
U _t	Equivalent threshold value of windspeed at 7 m (m/s)	11.32 (or site-specific)
F(x)	Function dependent on U _m /U _t derived using Cowherd (1985) (unitless)	0.194

A.6 Flux from Surface Water

The following equations estimate vapor flux from surface water and subsequent air exposure concentrations. The following equation estimates the chemical's tendency to partition into the air from water:

$$C_v = HC_w$$

Equation - R

where:

C_v	=	air concentration (g/cm ³)
H	=	Henry's Law constant (g/cm ³ -air)/(g/cm ³ -water)
C_w	=	water concentration (g/cm ³ -water)

The estimated air concentration must then be combined with a dispersion model such as those identified in Section A.2.3 or A.2.4 to estimate exposure concentrations.